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Effects of Chemical–Biological pretreatment of corn stalks on the bio-oils produced by hydrothermal liquefaction

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ABSTRACT

The production of bio-oils by hydrothermal liquefaction of lignocellulose is an attractive prospect. However, bio-oils produced using traditional methods have multiple components and are low grade, which limit their application. In this study, a new method was proposed to improve the quality of bio-oils. Chemical–Biological pretreatment (CB-pretreatment) was performed on fresh corn stalks to separate a partial lignin and to convert hemicellulose, generating ethanol for hydrothermal liquefaction and improving the quality of the resulting bio-oils. Furthermore, the influence of CB-pretreatment on the components of lignocellulose in corn stalks and the pretreated samples was analyzed. And the materials and bio-oils were analyzed with TGA and GC–MS. The results showed that the relative content of lignin reduced from 13.25 ± 0.87% to 8.97 ± 0.77% in the alkaline treatment. And the relative content of hemicellulose in the alkaline-acid pretreated substrates decreased from 21.65 ± 0.74% to 10.06 ± 0.48%. After the whole pretreatment, the concentrations of ethanol and remaining reducing sugar in the fermented liquor were 2.88 ± 0.09 mg/mL and 3.59 ± 0.30 mg/mL, respectively. Moreover, the pretreated substrates had a lower degradation temperature and less ash content than the corn stalks. The heating value of the bio-oil was 32.21 MJ/kg. Moreover, the number of bio-oils components was obviously reduced. Toluene and 2,6-di-tert-butyl-4-methylphenol, which are respectively used as high octane additive and antioxidant in fuels increased significantly in quantity, with their total percentage of corresponding peak area reaching 30.77%.

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1. Introduction

Shortage of traditional fossil fuels and problems such as environmental pollution and global warming [1] that arise as a result of fossil fuel consumption has become worldwide concerns. As a result, there is an urgent need for new liquid fuels [2,3]. Based on the characteristics of water under high temperature and pressure conditions, liquid bio-oils can be produced by hydrothermal liquefaction of biomass [4] through the destruction of the complex molecular structure of biomass and aggregating small molecules. This technology is regarded as the most promising bio-oils production technology to date [5,6]. The types of biomass used to produce bio-oils by hydrothermal liquefaction mainly consist of agricultural straw, wood waste, animal and vegetable oils, algae, animal waste, as well as municipal sludge. A number of studies [4,7,8] had shown that different types of biomass contain different components, such as lignocellulose, protein, and lipid, in varying amounts, and that the chemical compositions of the resulting bio-oils are also different, consisting of varying quantities of lipids, alcohols, phenols, ethers, ketones, acids and aromatic compounds. In general, lignocellulosic biomass contains cellulose, hemicellulose, lignin, extractives and ash [9]. Due to limited biomass resources, it is important to experiment with lignocellulosic biomass with relatively abundant reserves.

Factors that influence the bio-oils via hydrothermal liquefaction (HTL) include the type of raw materials, solvent, temperature, reaction time, and catalyst [10]. Raw materials and solvent determine the chemical composition of bio-oils, whereas reaction conditions mainly influence the quantity and pathway of bio-oils production. By investigating hydrothermal liquefaction of cellulose under acidic and neutral conditions, Yin et al. [11] found that the main products of hydrothermal liquefaction were furfural, as well as a small quantity of organic acids and dihydroxy acetone. Gosselink et al. [12] liquefied lignin in supercritical water to obtain phenolic and aromatic compounds. Peng et al. [13] studied hydrothermal liquefaction of corn stalks under CO atmosphere and found that the main products were aromatic compounds,

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phenols and fatty chain compounds. Li et al. [7] converted brown algae to bio-oils by hydrothermal liquefaction and detected 132 chemical compounds. The studies listed above showed that the more complex the original biomass, the more complex the resulting bio-oils chemical compositions profile. This could be attributed to the varying lignocellulose content in different biomass. And differences in the physical structure and chemical bond energy of lignocellulose components which are influenced by the species or living environment of the biomass also result in varying bio-oils chemical compositions. Those indicated that the characteristics of the raw biomass materials are the decisive factors in the final chemical composition of bio-oils, and the type of reactant also has a profound effect on the yield and chemical profile of the resulting bio-oils. Organic alcohols such as methanol and ethanol [14,15] are sometimes adopted as reaction solvents to help improve bio-oils yield and to reduce the oxygen content. Ethanol is widely used as reaction solvent [16,17]. Chen et al. [18] showed that using ethanol as the reaction solvent during hydrothermal liquefaction, esterification reactions occurred between ethanol (about 5%) and the organic acids that were generated during biomass breakdown, suggesting that only a small amount of ethanol can act as the reactant. Using ethanol as solvent may accelerate the biomass to bio-oils conversion [19] and increase the reaction efficiency.

In summary, it is clear that raw materials characteristics significantly influence on the chemical composition of bio-oils. When it was used as solvent, ethanol plays a key role in optimizing the chemical composition profile of bio-oils and increasing the reaction efficiency. Therefore, an efficacious pretreatment process for raw materials that helps adjust the contents of the raw components can be a simple way to improve the chemical composition of bio-oils. However, there are only a few studies about pretreatment of raw materials during bio-oils production using hydrothermal liquefaction. Therefore, the technology used in the cellulosic ethanol industry was applied to this work [20,21]. Lignocellulose was pretreated using chemical treatments and biological fermentation. This pretreatment method was denoted as “Chemical–Biological pretreatment” (CB-pretreatment) throughout this paper, and the bio-oils production method was named the “Chemical–Biological pretreatment Hydrothermal Liquefaction method” (CB-HTL). To investigate the influence of Chemical–Biological pretreatment on bio-oils production, the components and thermo-physical properties of the treated materials were analyzed, and the variation in the chemical composition profiles of the bio-oils was further compared.

2. Materials and methods

2.1. Materials and reagent

Fresh corn stalks with a moisture content of 66.2% were collected from the city of Shenyang. The corn stalks were thoroughly washed, frozen, stored at −10 °C, and thawed at room temperature before use. They were minced into particles <5 mm in size. NaOH, concentrated sulphuric acid, 3,5-Dinitro salicylic acid (DNS), potassium dichromate, methylene chloride, and acetone were analytical grade. The saccharomycetes used for fermentation was commercial Angel yeast (alcohol active dry yeast, Angel).

2.2. Chemical–Biological pretreatment

NaOH solutions (w/v) with concentration of 2%, as well as H_2SO_4 solutions with concentration of 3% were prepared. 30.00 g of the minced stalks were weighed and placed in 250 mL Erlenmeyer flasks. Then, 150 mL of the NaOH solutions with differing concentrations was added to every flask and kept at 40 °C in water bath for 0.5 h. The solutions were filtered using single-layer medical gauze and the treated biomass was rinsed with deionized water until the pH was neutral. The Erlenmeyer flasks were tilted to remove any remaining water. When no remaining water dripped from the flask, dilute H_2SO_4 solutions of 3% were added to the Erlenmeyer flasks, and the biomass was hydrolyzed in a boiling water bath (97 °C) for 1 h. And then the Erlenmeyer flasks were cooled with running water to room temperature and appropriate quantities of NaOH solutions were added to reach neutral pH to generate fermentation slurries. Dry yeast was revived using the method of adding dry yeast into 2% glucose water and incubating for 15 min in a 35 °C water bath. The amount of yeast was calculated as follows:

$$\text{Amount} = \frac{\rho_{yeast} \times v_{add}}{30} \times 1000‰ \tag{1}$$

where ρ_{yeast} was the concentration of yeast in the yeast mixture, V_{add} was the added volume, 30 was the mass of fresh corn stalks. Different volumes of the yeast mixture were added to the prepared fermentation slurries, and allowed to ferment at 35 °C for several days. After fermentation, all of the remaining matter in the Erlenmeyer flasks was used as raw materials for hydrothermal liquefaction.

2.3. Hydrothermal liquefaction

After fermentation, the volume of the slurry was adjusted to 200 mL before being placed in the reactor (KCFD 05-30). The reaction temperature was set at 370 °C and the reaction time was 30 min. After the reaction, the reactor was cooled to 25 °C and the exhaust valve was opened to exhaust gas generated during the reaction. Because the gas generated was mainly CO_2, it was not collected for further analysis [22]. The liquefaction products were collected and separated according to the process shown in Fig. 1. As shown in Fig. 1, the liquefaction products included gas, solid and liquid (including aqueous products and bio-oils). The reactor was then opened, and the aqueous products and some suspended solids were poured into a beaker (Beaker A). The reactor was washed with 100 mL of methylene chloride and 50 mL of acetone, and then the organic solutions and other solids were collected in a different beaker (Beaker B). Since the bio-oils was adsorbed together with residue and they were sticked in the wall and coil of reactor, the bio-oils were mainly extracted by the wash solution in beaker B. Firstly, the content of Beaker A was vacuum filtered using an organic membrane (0.45 μm) to separate the aqueous products and solid residues (Solid 1). The Erlenmeyer flask of the vacuum filter device was replaced by a new one. And the aqueous products were extracted with methylene chloride to get the organic solution. The organic solution in Beaker B was filtered under the vacuum filter with new flask to separate solids and organic solution. Bio-oils were designated as the remaining liquid of all the organic solutions after removing methylene chloride and acetone with rotary evaporation. The bio-oils yield is the ratio of the mass of bio-oils to the mass of dried corn stalks. The yield of liquid, solid and gas products of CB-HTL were calculated as follows:

$$Yield_{solid} = \frac{M_{solid}}{M_{driedCS}} \times 100\% \tag{2}$$

$$Yield_{liquid} = \frac{\rho \times V}{M_{driedCS}} \times 100\% \tag{3}$$

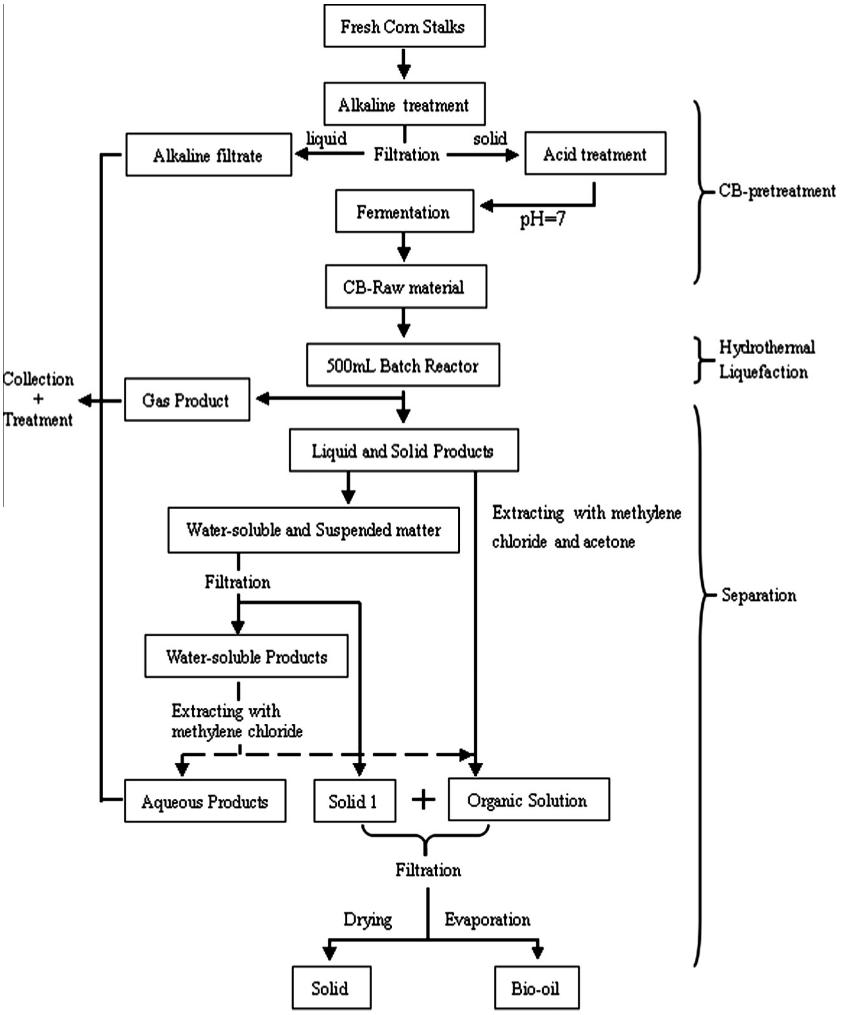

Fig. 1. Experimental procedure for CB-HTL process.

$$Yield_{bio-oil} = \frac{M_{bio-oil}}{M_{driedCS}} \times 100\% \qquad (4)$$

$$Yield_{gas} = 100\% - Yield_{solid} - Yield_{liquid} \qquad (5)$$

where $M_{dried\ CS}$ is the mass of the dried corn stalks, M_{solid} is the mass of the dried samples, ρ is the density of ethanol or sugar, V is the volume of liquid, $M_{bio\text{-}oil}$ is the mass of the bio-oil.

2.4. Analysis methods

2.4.1. The reducing sugar and ethanol analysis

Using a constant fermentation temperature (35 °C) and pH value (neutral), the influence of fermentation time and amount of yeast used were investigated. The results are shown in Figs. 2 and 3. The DNS assay [23] was employed to detect the

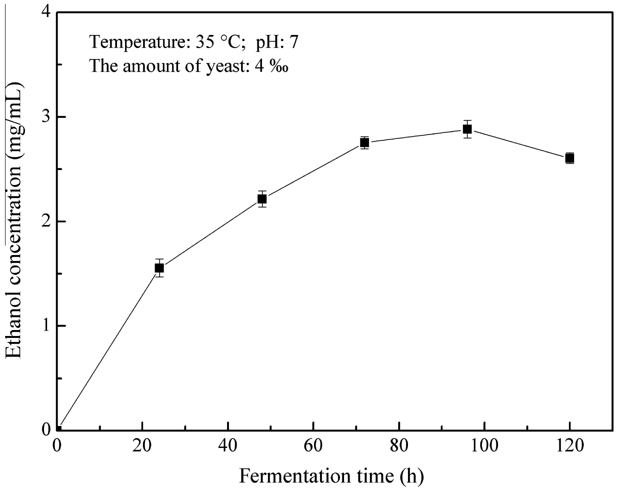

Fig. 2. Effects of fermentation time on ethanol concentration.

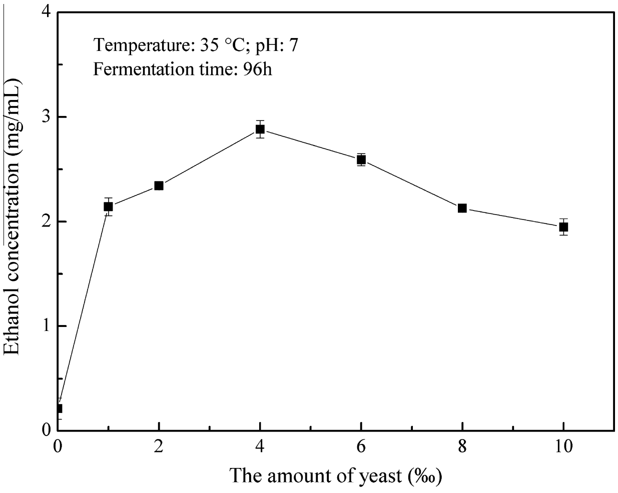

Fig. 3. Effects of the amount of yeast on ethanol concentration.

concentration of reducing sugar. Ethanol concentration detection used the potassium dichromate colorimetric method [24].

2.4.2. Other relevant measurements

Other relevant measurements of corn stalks samples at different stages of CB-HTL included the following experiments: hemicelluloses content, cellulose content and acid insoluble lignin content were determined by Van Soest Cellulose Content Determination Method [25,26] with the FIWE6 fibrometer system. Quantification method of ash was described as "Determination of Ash in biomass" [27].

Thermogravimetric analysis was performed using NETZSCH STA44 (high purity nitrogen carrier gas, temperature was increased from 50 °C to 750 °C at a rate of 10 °C/min, gas flow velocity 20 mL/min).

The chemical composition analysis of bio-oils was analyzed by GC–MS (Agilent 6890N/5975). The carrier gas was He at a flow rate of 1.0 mL/min. A HP-5 column (30 m × 0.25 mm × 0.25 μm) was used for the separation. For bio-oil analysis heating program was applied as follows: an oven isothermal program was set at 60 °C for 3 min, followed by a heating rate of 10 °C/min to 280 °C for 20 min. The injected volume was 1 μL. The identification of the peaks in the chromatogram was based on the comparison with standard spectra of compounds in the NIST library and/or on the retention times of known species injected. Quantification was done by the manual integration of the chosen single ion chromatogram.

The compositions of C, H, N, and S in the bio-oils were measured using a Flash 2000 series CHNSO analyzer (Thermo Scientific, USA). Oxygen content was then calculated by difference. The heating values of the bio-oils were determined using DuLong's formula:

$$HHV = 0.335 \times [C] + 1.423 \times [H] - 0.154 \times [O] - 0.145 \times [N] \qquad (6)$$

where [C], [H], [O], [N] are the mass fraction as showed in the Table 3.

3. Results and discussion

3.1. Analysis of CB-pretreatment on raw materials

3.1.1. The influence of fermentation conditions on ethanol concentration

Under fixed fermentation temperature (35 °C) and pH (neutral), the influences of fermentation time and the amount of yeast used were investigated (Figs. 2 and 3). With increasing fermentation time, the ethanol concentration increased steadily and peaked after 96 h fermentation. And then the ethanol concentrations decreased slightly with increasing fermentation time. Because angel yeast is a kind of mixed yeast (including a variety of fermentative bacteria), some fermentative bacteria may use ethanol as a carbon source [28] once the concentration of reducing sugar became insufficient at the end of fermentation. In Fig. 3, the reduction of ethanol concentration by them was more significant. With increasing amounts of yeast, the ethanol concentration increased continuously, and the highest ethanol concentration was 2.88 ± 0.09 mg/mL when the amount of yeast used was 4‰. Then the ethanol concentration decreased rapidly. This observation showed that the concentration of reducing sugar in the alkaline-acid treated slurry can provide sufficient carbon sources for anaerobic fermentation with lower yeast concentrations. However, when the number of yeast was excessive, a lot of carbon sources were used for yeast growth, which led to the available carbon source in the fermentation slurry could not support further ethanol production. After alkaline-acid hydrolysis, 96 h fermentation time and 4‰ yeast appeared to be the optimal fermentation conditions, under which the ethanol concentration was 2.88 ± 0.09 mg/mL, and the remaining reducing sugar concentration was 3.59 ± 0.30 mg/mL. The ethanol yield was 4.26% and the sugar utilization rate was 71.56% which were all lower than that has been reported [29–31], because the major purpose of CB-pretreatment was to adjust the composition of biomass materials.

3.1.2. The influence of CB-pretreatment on raw materials components

Fig. 4 shows the variations observed in the relative contents of cellulose, hemicellulose and lignin in corn stalks (CS), alkaline treated substrate (AS), alkaline-acid treated substrate (AAS) and alkaline-acid-fermentation treated substrate (AAFS), and all the samples were dried at 105 °C. The mass balance analysis of BC-HTL process was showed in Table 1. Fig. 4 showed that the content of lignin in relation to corn stalks decreased from 13.25 ± 0.87% to 8.97 ± 0.77%, which may be attributed to the reaction between NaOH and lignin, and a partial of phenols were dissolved [32]. As the first step of chemical treatment, soaking in an alkaline solution may destroy the structure of lignocellulose, and expose the cellulose and hemicellulose which were protected by lignin to allow access for further treatment. After alkaline-acid treatment, the content of hemicellulose in relation to corn stalks decreased significantly from 21.65 ± 0.74% to 10.06 ± 0.48%, which may be because hemicellulose were hydrolyzed by the dilute H_2SO_4 [19] when the reaction temperature reached 100 °C, which resulted in its breakdown into xylose [33]. And, cellulose was affected slightly during the acid hydrolysis stage. Reactions in the fermentation treatment mainly involved inversion of reducing sugar in the slurry into ethanol, so the changes in lignocellulose components were not

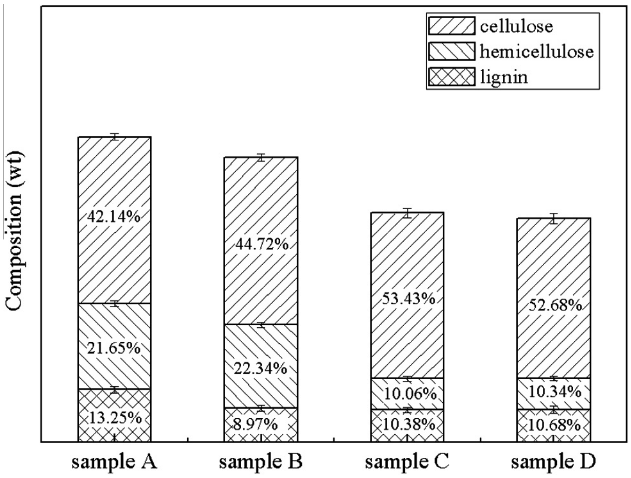

Fig. 4. Effects of different stages of processing on chemical composition. Sample A: corn stalk samples; Sample B: alkaline treated samples; Sample C: alkaline-acid treated samples; Sample D: alkaline-acid-fermentation treated samples.

Table 1
The mass balance analysis of CB-HTL process.

Samples	Solid %[a]	Liquid %		Others %[b]
		Ethanol %	Sugar %	
CS	100	Nd	Nd	0
AS	93.53	0	1.55	4.92
AAS	76.31	0	18.67	5.02
AAFS	76.75	4.26	5.31	15.60
HTL	8.39	37.95[c]		53.66

Nd not determined
[a] Dry weight bass.
[b] Calculated by difference.
[c] Bio-oils yield.

obvious. Besides, the ash contents in corn stalks and the CB-pretreatment samples were 4.75 ± 0.15% and 2.24 ± 0.27%, respectively. The reducing of the ash content was caused by the removal of water-soluble ash after alkaline treatment process. And the less ash content meant the higher conversion because ash was difficult to be liquefied [34].

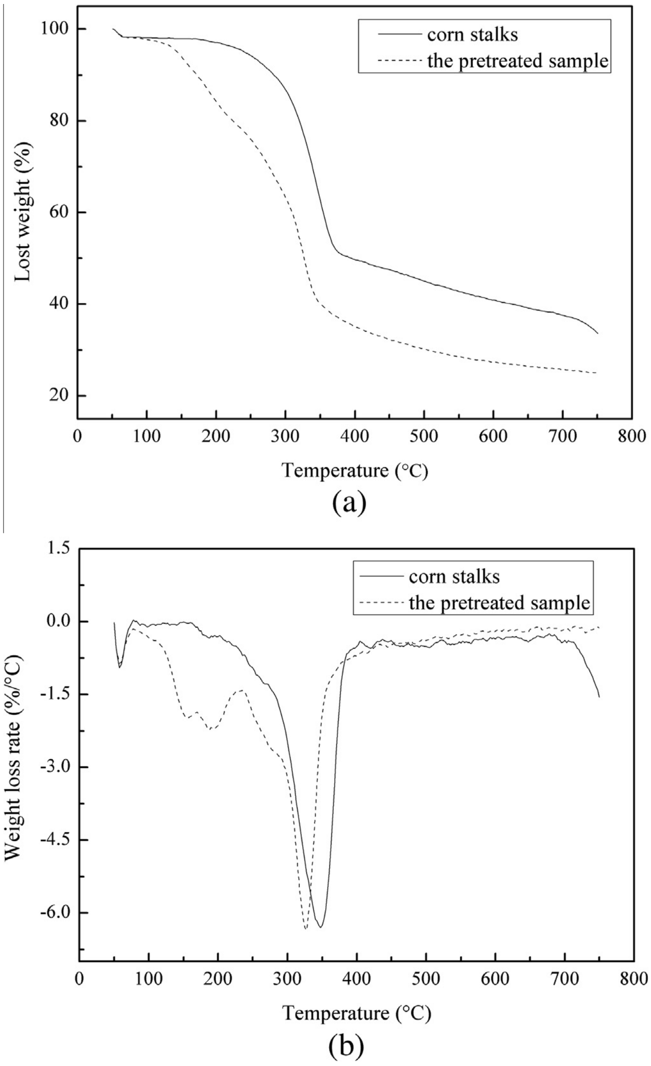

Fig. 5. Comparison of TGA and DTG curves for corn stalks and the alkaline-acid-fermentation treated samples. (a) TGA curves; (b) DTG curves.

3.1.3. TG and DTG analysis

TG and DTG analysis were conducted on both corn stalks and the pretreated samples to better understand the thermal degradation behavior of each sample. Fig. 5 shows the TGA and DTG curves respectively. Clearly, the TGA and DTG curves of corn stalks and the pretreated samples are significantly different due to their great differences in chemical composition as showed in Fig. 4. Fig. 5a shows that the main range of weight loss for the pretreated samples was from 125 °C to 370 °C, while that was from 200 °C to 380 °C for corn stalks. It can be found that the initial degradation temperature of the pretreated samples was lower than that of corn stalks. In the range of 125–226 °C (Fig. 5a), the weight loss of corn stalks was only 1.97%, whereas it was 17.16% for the pretreated sample in this range. According to Yang [35], thermal breakdown of the three main components of lignocellulose are as follows: hemicelluloses > cellulose > lignin. Chen's study [36] showed that hemicellulose and cellulose decomposition peaks were seen at around 237 and 327 °C, respectively. So the lower hemicellulose content in pretreated samples was likely the main reason for the higher loss of mass during the initial thermolysis stage. Moreover the reduction of hemicellulose made a contribution to destroying the structure of lignocellulose and weakened the self-protection of biomass, which led to a lower temperature for thermal decomposition. From 260 to 370 °C, both samples experienced significant variation in weight loss. The stage at which the thermolysis of cellulose occurred was consistent with a previous report in which cellulose began thermolysis in the range of 283–370 °C [37]. At temperatures higher than 370 °C, the rate of weight loss in both corn stalks and pretreated samples were more or less consistent. At this stage, the weight loss is mainly due to the breakdown of lignin [38].

3.2. Analysis of bio-oils components

The yield of HTL oil and CB-HTL oil were 30.85% and 37.95%, respectively, indicating that the CB-HTL could improve the bio-oils yield. The chemical compositions of bio-oils produced by the pretreated samples and the untreated samples were measured using GC–MS and the total ion chromatograms of bio-oils are shown in Fig. 6. The derived compounds those relative contents were more than 0.5% were listed in Table 2. The Table 3 showed the elemental composition and heating value of the bio-oils. Most of the peak

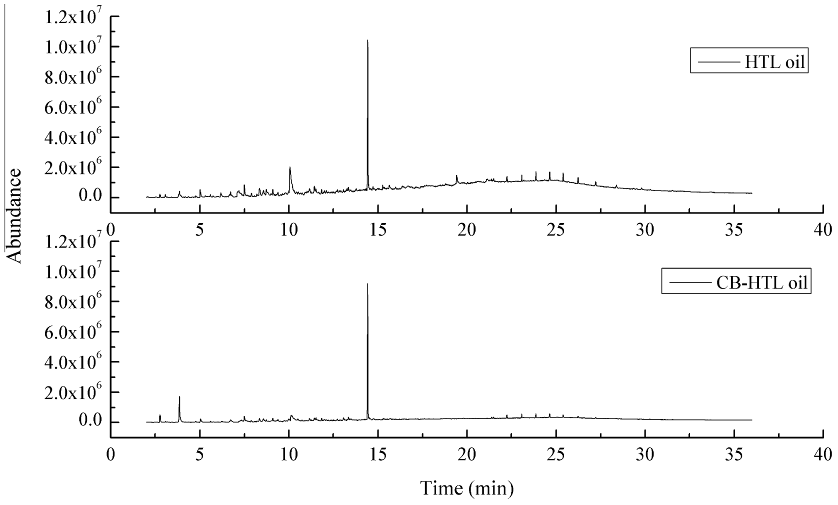

Fig. 6. Comparison of the total ion chromatograms of HTL oil and CB-HTL oil.

Table 2
The major organic compounds in different bio-oils.

Chemical family	Compounds	Relative content (% area)	
		HTL oil	CB-HTL oil
Hydrocarbons	Toluene	0.50	2.55
	Indane	–	0.75
	Indene	–	0.63
	1-Methylcyclooctene	–	0.56
	1H-Indene, 3-methyl-	1.42	1.58
	Benzene, 1-Methyl-4-(1-propyn-1-yl)-	–	1.32
	2-Methylbicyclo[4.3.0] non-1(6)-ene	–	1.41
	9-Hexylheptadecane	–	0.92
	Nonadecane	3.15	–
	Tetracosane	–	0.67
	Pentacosane	3.56	–
	Octacosane	3.24	0.84
	Tetratetracontane	2.93	–
	Heptacosane	1.43	1.08
	Octadecane,3-ethyl-5-(2-ethylbutyl)-	–	0.85
Ketones	2-Cyclopenten-1-one,2,3,4-trimethyl-	5.04	1.05
	Cyclopentanone	0.55	
	4-Hydroxy-4-methyl-2-pentanone	1.29	10.91
	2-Cyclopenten-1-one,2-methyl-	1.63	1.75
	3,4-Dimethyl-2-cyclopenten-1-one	–	0.62
	2-Cyclopenten-1-one,3,4-dimethyl-	–	2.18
	2-Methylcyclopentanone	0.61	–
	3-Methylcyclopentanone	0.53	–
	3-Methyl-2-cyclopenten-1-one	1.38	0.76
	2-Cyclopenten-1-one,2,3-dimethyl-	4.02	1.91
	2-Cyclohexen-1-one,4,4-dimethyl-	–	2.18
	2-Cyclopenten-1-one,3-(1-methylethyl)-	–	1.93
	1-Methylcyclooctene	0.62	
	2-Cyclohexen-1-one,4-ethyl-4-methyl-	–	2.82
	3,5,5-trimethyl-3-cyclohexen-1-one	–	2.02
	2,3-Dihydro-1H-inden-1-one	–	1.52
	2(3H)-Benzofuranone, hexahydro-3-methylene-	3.07	–
	1H-Inden-1-one,2,3-dihydro-2-methyl-	–	1.06
	7-Methyl-indan-1-one	–	1.16
	1-Indanone	1.78	–
	1H-Inden-1-one,2,3-dihydro-3,3-dimethyl-	1.10	1.23
Phenols	Phenol	1.64	–
	4-Ethylphenol	15.44	10.14
	4-Ethyl-2-methoxyphenol	2.41	1.43
	2,6-Di-tert-butyl-4-methylphenol	20.13	28.22
Aldehydes	5-Ethyl-2-furaldehyde	–	1.75
	3-Cyclohexene-1-carboxaldehyde,2,4,6-trimethyl-	–	1.17
	Cinnamaldehyde	3.03	–
Organic acids	n-Hexadecanoic acid	1.91	–
Total		82.41	88.97

Table 3
Elemental compositions of HTL oil and CB-HTL oil.

Samples	Elemental composition (wt%)				O/C	H/C	HHV (MJ/Kg)
	C	H	O[a]	N			
HTL oil	65.47	8.24	25.45	0.84	0.29	1.51	29.62
BC-HTL oil	67.13	9.37	23.15	0.35	0.26	1.67	32.21

[a] By difference

identities are necessarily tentative, which are based solely on the inspection of the MS fragmentation patterns and their best matches with mass spectra stored in the computer library. Fig. 6 shows that the chemical complexity of bio-oils produced by CB-HTL of corn stalks decreased significantly, while the quantities of generated compounds were relatively high, indicating that CB-pretreatment helped alter the chemical compositions of the resulting bio-oils and promoted the production of certain desirable chemicals. The main reason for the reduction of chemical complexity is that the complex hemicellulose structure [19] in the untreated materials was destroyed through CB-pretreatment, while reducing sugar and ethanol which have simplified structures were produced. Therefore, the complex hemicellulose fragments were substantially reduced during hydrothermal liquefaction, and the active fragments from breakdown were mainly from cellulose and lignin.

As shown in Table 2, the bio-oils produced by CB-HTL mainly contained ketones, hydrocarbons and phenols. The ketones were produced during breakdown and cyclization of cellulose, while the ethanol produced by fermentation played an active role in the synthesis of ketones [39]. The phenols mainly originated from the breakdown of lignin. Compared to direct hydrothermal liquefaction of biomass, bio-oils produced by CB-HTL contained 5.10, 8.46 and 1.40 times (the rate of percentage of relative peak area) more toluene, 4-hydroxy–4-methyl-2–pentanone and 2,6-di-tert-butyl-4-methylphenol, respectively. The content of 2,6-di-tert-butyl-4-methylphenol, namely BHT, a common antioxidant used in food and liquid fuels [40] reached 28.22%, and it was the major component in the bio-oils produced using the CB-pretreatment hydrothermal liquefaction method. Secondly, the content of 4-hydroxy-4-methyl-2-pentanone, which can be used as the raw materials in the production of antifreeze, was 10.91%. Toluene is a common additive in high octane gasoline [41] and its percentage of relative peak area increased from 0.50% to 2.55% from the untreated to the pretreated sample. The percentage of corresponding peak area of three substances above accounted for 41.68%, which represents an enormous improvement in the value of the bio-oils. In addition, the heating value of CB-HTL oil was higher than that of HTL oil, and was also higher than that of bio-oils liquefied directly using lignocellulosic biomass, such as cornelian cherry stones [42], algal biomass [43], and cypress [44].

4. Conclusion

Chemical–Biological pretreatment Hydrothermal Liquefaction method for bio-oils production was tested in this study. It not only provided the necessary ethanol reactant for hydrothermal liquefaction, but also was beneficial in improving the quality of the resulting bio-oils. This technique represents a feasible new route for bio-oils production by hydrothermal liquefaction of lignocellulosic biomass.

After Chemical–Biological pretreatment of fresh corn stalks, the concentration of reducing sugar in the fluid portion was 3.59 ± 0.30 mg/mL, and the ethanol concentration was 2.88 ± 0.09 mg/mL. The pretreated substrate, which consisted of 52.68 ± 1.24% of cellulose, 10.34 ± 0.55% of hemicellulose, and 10.68 ± 0.89% of lignin, became the better materials for the production of bio-oils by hydrothermal liquefaction.

Chemical–Biological pretreatment could reduce the chemical complexity of the resulting bio-oils and improve the yield of several desirable chemical compounds. The total percentage of peak area of toluene and 2,6-di-tert-butyl-4-methyl-phenol were 30.77%, which can be used as additive and antioxidant respectively. The heating value of the CB-HTL oil was 32.21 MJ/kg, compared with 29.62 MJ/kg for the HTL oil.

Acknowledgements

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